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Silica Gel as a Catalyst in Organic Reactions

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE
JOHNS HOPKINS UNIVERSITY IN CONFORMITY WITH
THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
JUNE, 1930

BY
JAMES ALBERT MITCHELL

BALTIMORE:
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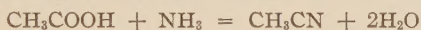
He also wishes to express his gratitude to Professors J. C. W. Frazer, W. A. Patrick, G. H. Cartledge, F. O. Rice and D. H. Andrews, and to Doctors Wm. M. Thornton, Jr., and E. Ott for their valuable instruction and help in the lecture room and laboratory. The author feels especially indebted to Professor G. H. Cartledge and Doctor Wm. M. Thornton, Jr., whose early training and instruction filled him with an enthusiasm for chemistry and have been a constant source of inspiration throughout his career as a student at Hopkins.



SILICA GEL AS A CATALYST IN THE PREPARATION OF NITRILES

Previous investigations have shown that silica gel is an excellent catalyst for certain dehydrating reactions involving organic compounds. Milligan, Chappell and Reid¹ showed it to be an extraordinarily good esterification catalyst; Brown and Reid studied its application in the alkylation of ammonia and dehydration of alcohols² and also in the alkylation of aniline.³

The catalytic dehydration of the nascent amide formed from acetic acid and ammonia, according to the equation



in the presence of thoria and alumina, has been studied by Van Epps and Reid.⁴ They found that an 85% yield of nitrile could be obtained at 500° with the better catalyst, alumina. They reported that no nitrile was obtained by passing ethyl acetate and ammonia over alumina, while Mailhe⁵ obtained nitriles from esters and ammonia with both thoria and alumina.

This reaction has been investigated in the presence of silica gel.

Results

We have found that silica gel is a more efficient catalyst than either thoria or alumina in the preparation of nitriles from acids and ammonia. Using acetic acid and an excess of ammonia, as the temperature of operation is raised the percentage conversion to acetonitrile increases until at 500–525° a maximum is reached (practically quantitative). Increasing the temperature to 550° results in a decreased yield and increasing it to 575° lowers the yield still further. It appears that operation at tempera-

¹ Milligan, Chappell and Reid, *J. Phys. Chem.*, **28**, 872 (1924).

² Brown and Reid, *ibid.*, **28**, 1067, 1077 (1924).

³ Brown and Reid, *J. Am. Chem. Soc.*, **46**, 1836 (1924).

⁴ Van Epps and Reid, *ibid.*, **38**, 2128 (1916).

⁵ Mailhe, *Bull. soc. chim.*, [4] **23**, 232 (1918); *Ann. chim.*, [9] **13**, 213 (1920).

tures above 500° fouls the catalyst, for after such treatment runs at lower temperatures gave low yields.

If the temperature of operation was not allowed to rise above 500° the catalyst was very slightly discolored and its activity continued unimpaired almost indefinitely, even after repeated heating and cooling in air.⁶

In every case when the temperature of operation was above 500° a noticeable quantity of a white solid formed in the condenser when distilling the lower (water) layer of the product. The higher the temperature the greater was the yield of this material. It was identified as ammonium carbonate. It is reasonable to suppose that even at temperatures of 500° or lower some ammonium carbonate is formed—which may account, in part, for the salting out of the nitrile to form the upper layer. The acetic acid not converted to nitrile or amide is, of course, in the lower layer in the form of ammonium acetate, and is also efficient as a salting out agent.

A rough calculation of the velocity of passage of the reactants through the catalyst in the case of acetonitrile shows that when the time of contact is twenty-five seconds at 500° , the percentage conversion is 95% (practically quantitative) and only 60% when the rate of flow of the reactants is twice as fast.

The results obtained show that highly purified gel and commercial gel are of the same order of activity.

All the aliphatic acids from acetic to heptonic, with an excess of ammonia, produce large yields of nitriles. The yield from lauric acid is decidedly lower and no nitrile has been obtained from palmitic acid. High yields of nitriles are also obtained from phenylacetic and hydrocinnamic acids.

With all the acids except acetic and isovaleric the catalyst blackens readily at temperatures of 500° or lower and loses its activity in most cases very gradually with use.

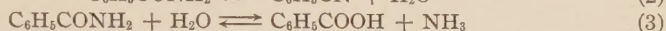
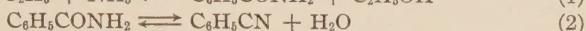
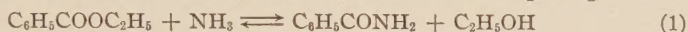
The yields of isovaleronitrile, above 90%, offer a rather surprising contrast with the yield of *n*-valeronitrile, which never exceeded 80%. The difference can hardly be ascribed to any difference in thermal stability of the two acids and, as the nitriles are relatively more stable than the acids, the results may indicate that the formation of nitrile from the isovaleric acid is much more rapid than from the normal acid.

In passing an ester with an excess of ammonia over silica gel the initial percentage conversion to nitrile is high, approximately the same as with the acid. The catalyst, however, in contrast with the acid reaction, is rapidly fouled. Aside from the greater instability of the ester as compared with the acid, the fouling of the catalyst might be partially explained by the decomposition products of the alcohol formed in the ester reaction.

⁶ With thoria and alumina the catalytic efficiency has been shown to fall off fairly rapidly with use.

Brown and Reid⁷ have shown that large amounts of aldehyde are formed in passing butyl alcohol over silica gel. Our experience indicates that silica gel is rapidly fouled in any reaction involving the presence of aldehyde, probably due to the formation of polymerization products.

In passing ethyl benzoate and ammonia over silica gel, ammonium benzoate was obtained as one of the products of the reaction. In this instance we are dealing, after the initial reaction (1), with two competing reactions



The fouling of the catalyst has been found to favor Reaction 3 (*i. e.*, more ammonium benzoate is formed) and decrease the yield of nitrile, Reaction 2. If the catalyst is effective in the establishment of both equilibria (2) and (3), it is only reasonable to expect that if it becomes less effective in one reaction it will also become less effective in the other. Two alternative explanations of the experimental result are possible: first, either the gel is *such an effective catalyst* for the establishment of equilibrium, (3) that partial fouling hardly impairs its activity, or, second, the hydration of the amide and dehydration of the ammonium salt, (3), is *independent of the catalyst* and merely involves a thermal equilibrium. As less amide is converted to the nitrile more is available for hydrolysis to the acid and ammonia.

In order to ascertain which of these two explanations is correct, benzamide was hydrolyzed in sealed tubes with and without silica gel. The gel had no effect on the rate of hydrolysis. Similar experiments using ammonium acetate showed that silica gel has no influence on the rate of formation of the amide.

It is evident, therefore, that silica gel affects only the second reaction, in the conversion of acids and ammonia to nitriles.

It is, of course, a well-known fact that ammonium salts of the aliphatic acids are easily dehydrated to the amide by the application of heat. Boehner and Andrews⁸ and Boehner and Ward⁹ have shown that various large-surface catalysts are active in the dehydration of amides. In our experiments in which amides were swept over silica gel by a current of air or nitrogen at temperatures above 400° very high yields of nitriles were obtained.

Experimental

Apparatus and Procedure.—The horizontal tube furnace used was similar to that described by Kramer and Reid.¹⁰

⁷ Brown and Reid, *J. Phys. Chem.*, **28**, 1080 (1924).

⁸ Boehner and Andrews, *J. Am. Chem. Soc.*, **38**, 2503 (1916).

⁹ Boehner and Ward, *ibid.*, **38**, 2505 (1916).

¹⁰ Kramer and Reid, *ibid.*, **43**, 880 (1921).

The catalyst, 100 g. of silica gel, was placed in a pyrex tube approximately 56 cm. by 23 mm. and activated by heating for four or five hours at 210° in a slow current of dried air, gradually raising the temperature to that desired in the experiment, while continuing the current of dried air.

An accurately measured quantity of acid (or ester) was passed through a dropping arrangement, the flow of which could be regulated by means of a glass rod ground in the tip, and introduced directly by a capillary into an atmosphere of ammonia, over the gel. The ammonia was passed through a calibrated flowmeter and led in through a separate tube ending a little short of the end of the capillary tube. An excess of ammonia was always used.

The temperature was read from a thermometer placed between the catalyst tube and the wall of the furnace and kept constant within 1° . Temperatures above 500° were read with a thermocouple.

The gases after leaving the catalyst were led through a condenser, cooled by very cold water, and thence into a receiver, which in the case of acetonitrile was immersed in an ice-salt bath. The excess ammonia was allowed to escape.

The product invariably separated into two layers—the upper layer being practically pure nitrile and ammonia. The nitrile is salted out by ammonium acetate and ammonium carbonate. The lower layer in the case of the soluble nitriles also contained considerable nitrile.

Analysis.—Van Epps and Reid⁴ estimated acetonitrile by fractional distillation. The product obtained, however, cannot be freed completely from ammonia, even after refluxing for some time.

The following analytical method proved very satisfactory. The two layers from the run were separated and distilled separately from a Claisen flask with an extended neck and the distillates collected up to 90° . The combined distillate from both layers was weighed and entered as product. The acetonitrile present was determined as follows. An accurately weighed sample of the product (about 0.5 g.) was sealed in a glass tube with 2 cc. of 18 *N* sulfuric acid and heated at 150° for two and one-half to three hours. The tube contents, after hydrolysis, were carefully washed into a 50-cc. volumetric flask. A 5-cc. aliquot was titrated for total acidity with 0.1 *N* sodium hydroxide with phenolphthalein as an indicator, using throughout carbon dioxide-free water. A similar 5-cc. aliquot was heated in a porcelain dish on a water-bath for one and one-half hours, frequently washing down the sides of the dish with distilled water. The acetic acid formed by the hydrolysis of the nitrile was volatilized, leaving the excess sulfuric acid behind. The residue was titrated as before. The difference in the titers, of course, represents the acetic acid present—whence the acetonitrile in the product can be calculated. The estimation of propionitrile was effected in much the same manner. The two-layer product from the run was saturated with potassium carbonate. This effectively salted out the nitrile (an aqueous solution of propionitrile saturated with potassium carbonate retains in solution only about 0.02 g. per cc.). The upper layer was separated, distilled, and the fraction boiling between 90 – 98° analyzed as before.

Several similar analyses were run on butyronitrile, but this and the higher nitriles were easily purified and quickly freed of ammonia by distillation. Accordingly the higher nitriles were purified and estimated by fractional distillation.

Catalyst.—The catalyst used for the most part was ordinary 8–14 mesh commercial gel.¹¹ A purified gel catalyst was prepared by refluxing a sample of the commercial gel for several hours with concentrated nitric acid and subsequently cleaned by continued washing with distilled water until it was snow-white and acid free. A portion of the

¹¹ Kindly furnished by Professor W. A. Patrick.

gel purified in this manner was further purified by electrolysis, until entirely freed of electrolyte.¹²

Materials.—The acetic acid was C. P. glacial acetic acid. The propionic, butyric and caproic¹³ acids were technical materials carefully purified by distillation through a precision fractionating column. The isovaleric, lauric, palmitic and phenylacetic acids, butyl acetate and ethyl benzoate employed were the purest materials obtainable from the Eastman Kodak Company. The normal valeric acid used was prepared by the Grignard reaction from *n*-butyl bromide and carbon dioxide and purified by distillation through a fractionating column. Normal heptioic acid was prepared by oxidizing heptaldehyde with chromic acid mixture, separating the product formed and purifying by fractionation through a column.

Hydrocinnamic acid was prepared by completely reducing pure cinnamic acid with amalgamated zinc according to the method of Clemmensen¹⁴ and recrystallizing the product from water until an accurate, sharp melting point was obtained.

n-Butyl *n*-butyrate was prepared by the oxidation and esterification of *n*-butyl alcohol with sulfuric-chromic acid.¹⁵

TABLE I
ACETONITRILE

Temp., °C.	Acid used, g.	Time of expt. min.	Rate of flow of ammonia, cc./min.	Amount, g.	Product Purity, %	Yield, %
Effect of variation in temperature						
400	26.0	72	100	15.08	84	71
450	26.0	70	100	17.06	91	87
500	26.0	70	100	19.20	90	97
525	26.0	70	100	19.19	89	96
550	26.0	69	105	18.11	81	82
575	26.0	70	105	17.62	78	77
500	26.0	72	105	16.00	94	84
550	26.0	66	110	15.33	85	73
500	26.0	75	100	15.77	89	78
Effect of variation in rate of flow						
500	26.0	74	110	18.13	85	87
500	26.0	80	150	17.60	79	78
500	26.0	71	180	17.44	81	79
500	26.0	105	150	14.28	92	74
500	26.0	30	230	11.83	89	60
500	26.0	89	105	18.43	85	88
500	26.0	110	100	20.30	87	98
500	26.0	100	80	19.58	83	91
Gel purified by nitric acid and electrolysis						
500	31.0	77	105	21.07	92	92
500	26.0	75	110	19.37	84	91
500	26.0	75	110	17.37	89	87
500	26.0	72	105	17.27	93	90

¹² Using the method described by O. G. Bennett, "Dissertation," Johns Hopkins University, 1930.

¹³ Kindly furnished by Sharp and Dohme, Baltimore, Md.

¹⁴ Clemmensen, *Ber.*, **46**, 1837 (1913); **47**, 51, 681 (1914).

¹⁵ "Organic Syntheses," John Wiley and Sons, Inc., New York, 1925, Vol. V, p. 23.

The Preparation of Nitriles from Acids

Acetonitrile (Methyl Cyanide).—The effect of variation of temperature on the yield of nitrile is indicated in the first section of Table I.

Variation in the rate of flow of the two reactants was studied and the results are tabulated in Section II, Table I. Keeping the temperature constant at 500° it is evident, as is to be expected, that the time of contact with the catalyst is a factor of considerable importance. Increasing the rate of flow of either the acid or ammonia results in a decreased yield.

The results obtained in using a highly purified sample of the same gel are indicated in the third section of Table I. It is evident that similar yields of nitriles are obtained.

Each section of the table represents the results from a fresh charge of catalyst.

The two-layer product from the run was always water white without the least discoloration.

Propionitrile (Ethyl Cyanide).—The product, which always separated into two layers, was almost colorless, although several times a slight yellow coloration was apparent. After salting out with potassium carbonate, the upper layer upon distillation was quickly freed of ammonia and the boiling point rose rapidly to 95°. The fraction was taken between 90–98°—the major portion distilled between 95–97°. The propionitrile occasionally smelled faintly of ammonia, generally not at all, and the analyses showed a high degree of purity (98%).

TABLE II
PROPIONITRILE

Temp., °C.	Acid used, g.	Time of expt., min.	Rate of flow of ammonia, cc./min.	Product Amount, g.	Purity, %	Yield, %
450	24.5	77	100	14.90	99	81
500	24.5	69	100	15.53	98	83
500	24.5	76	105	15.07	97	80
500	24.5	101	90	15.37	99	83
410	24.5	63	115	10.00	94	51
450	24.5	70	110	12.60	100	69
A new catalyst						
500	24.5	92	95	15.87	98	85
500	24.5	104	90	16.47	98	88
500	24.5	108	85	15.97	98	86

Laurnitrile (*n*-Undecyl Cyanide).—Ninety grams of lauric acid was passed over commercial gel at 500° with an excess of ammonia. The rate of flow was comparable with those of the other experiments. The acid was kept molten by surrounding the dropping apparatus with a "chimney," through which a current of hot air was passed. The temperature was kept constant (65°) to insure an even flow of acid.

TABLE III
 HIGHER NITRILES

Temp., °C.	Acid used, g.	Time of expt., min.	Rate of flow of ammonia, cc./min.	Product, g.	Yield, %
<i>n</i> -Butyronitrile					
450	23.7	65	100	15.24	82
500	23.7	105	100	17.57	94
500	23.7	68	100	17.00	91
500	26.0	113	90	19.00	93
450	23.7	63	110	14.37	77
500	23.7	71	110	16.37	88
500	23.7	84	80	16.88	90
<i>n</i> -Valeronitrile					
500	44.0	134	95	27.10	76
500	22.0	92	80	14.40	80
500	22.0	105	80	14.60	81
510	22.0	80	90	13.00	73
Isovaleronitrile					
500	23.0	75	90	16.9	90
500	23.0	89	95	17.3	92
500	23.0	114	85	17.7	94
500	23.0	84	85	17.4	93
<i>n</i> -Capronitrile					
500	26.7	98	80	19.90	89
500	24.0	89	90	17.97	88
500	25.3	105	100	18.80	89
500	24.0	78	90	18.30	90
500	24.0	62	105	17.14	84
500	24.0	117	85	18.88	93
<i>n</i> -Heptonitrile					
500	22.6	90	95	17.72	92
500	22.6	73	100	18.30	94
500	22.6	54	90	17.65	91
500	45.2	141	90	36.00	93

A fair amount of solid material was obtained in the product, which seemed to consist of the amide, and the ammonium salt of the acid.

The liquid product was washed with water and distilled under 98 mm. pressure. The larger part of the material distilled at 192–195°; yield of nitrile, 46.0 g. (55%).

Palmitic acid was passed over silica gel at 500° with an excess of ammonia. The acid was kept molten and at a temperature of 90°, using the same technique as with the lauric acid. The product was distilled under diminished pressure. The major portion distilled within 1.5 of 265° under 32 mm. pressure. It appeared to be a mixture of the amide and the acid. The product after several recrystallizations was still very impure

and melted sluggishly around 40° . No noticeable amount of nitrile was obtained.

Phenylacetonitrile (Benzyl Cyanide).—One hundred and fifty grams of phenylacetic acid was passed over commercial gel at 500° with an excess of ammonia at a rate comparable to those in the previous experiments. The acid in the dropping arrangement was kept molten and at a temperature of 90° as before. The product separated into two layers. The upper (nitrile) layer was separated and distilled under vacuum. The product was almost pure nitrile. That fraction boiling between 128.5 – 129.5° at 31 mm. was entered as nitrile; yield, 112 g. (87%). The gel was completely blackened after use, but was still active.

Phenylpropionitrile (Phenylethyl Cyanide).—One hundred and twenty-three grams of hydrocinnamic acid was passed over commercial gel at 500° with an excess of ammonia, using the same technique as in the previous experiments with solid acids. The upper layer was distilled as before, practically all of it distilling at 141 – 142° at 25 mm.; yield of nitrile, 87 g. (81%).

The Preparation of Nitriles from Esters

Acetonitrile from *n*-Butyl Acetate.—The results obtained upon passing *n*-butyl acetate over commercial gel with an excess of ammonia are indicated in Table IV. Each space in the table indicates a change in catalyst.

TABLE IV
ACETONITRILE FROM *n*-BUTYL ACETATE

Temp., $^{\circ}\text{C.}$	Ester used, g.	Time of expt., min.	Rate of flow of ammonia, cc./min.	Product Amount, g.	Purity, %	Yield, %
500	21.8	64	95	9.64	70	87
444	21.8	47	100	9.80	65	82
400	21.8	77	95	10.50	59	80
400	21.8	81	90	10.22	46	61
370	45.3	129	90	11.17	59	41
404	43.6	112	90	12.17	47	37
370	43.6	120	90	12.00	52	40
400	43.6	120	85	14.57	52	49
455	43.6	112	95	15.82	61	63
455	43.6	123	105	14.60	55	52

The two layers of the product, highly colored and fluorescent, were separated and each distilled up to 85° . The material was analyzed for nitrile in the same manner as was the product obtained from acetic acid. At 500° the efficiency of the catalyst decreased rapidly. At lower temperatures the life of the catalyst was longer, but its decline was still marked.

***n*-Butyronitrile from *n*-Butyl *n*-Butyrate.**—Here again it is evident that good yields of nitrile are obtainable with a fresh catalyst, but the efficiency drops off rapidly with use (Table V, Section I).

Benzonitrile from Ethyl Benzoate.—As the use of benzoic acid was precluded by the type of apparatus employed, ethyl benzoate was passed over silica gel with an excess of ammonia gas. The formation of nitrile from the ester may be taken as sufficient indication that it is also obtainable from the acid. The results of experiments with ethyl benzoate are noted in Table V, Section II. It is apparent that favorable yields may be obtained. The catalyst, as with the other esters, is rapidly fouled.

The product invariably separated into two layers. The lower (nitrile) layer was distilled. The boiling point rapidly rose to 190° and practically all of the layer boiled between 190–195°. This fraction was taken as nitrile.

It was observed that during the experiments a considerable quantity of white solid collected in the condenser. As the catalyst was used and its efficiency decreased, the yield of this material increased. These crystals, upon examination, proved to be ammonium benzoate.

TABLE V
EXPERIMENTAL DATA

Temp., °C.	Ester used, g.	Time of expt., min.	Rate of flow of ammonia, cc./min.	Product, g.	Yield, %
<i>n</i> -Butyronitrile from <i>n</i> -Butyl <i>n</i> -Butyrate					
380	43.4	96	90	11.00	53
410	45.1	122	85	12.50	58
450	43.4	123	80	13.51	65
500	43.4	102	95	15.49	75
450	43.4	113	80	11.70	56
Benzonitrile from Ethyl Benzoate					
500	26.3		90	12.0	66
440	52.6	125	70	24.0	66
420	26.3	60	70	10.8	60
455	26.3	70	65	14.0	77
410	26.3	60	90	7.4	41
455	26.3	65	80	8.1	45

The Influence of Silica Gel on the Amide-Ammonium Salt Equilibrium.—Exactly weighed quantities of purified benzamide (0.3–0.4 g.) and a weighed quantity of water (about 1.1 g.—a large excess of water was used to force the hydrolysis of the amide) were sealed in pyrex tubes, half of the tubes containing about 0.5 g. of activated silica gel. Pairs of tubes with and without gel were heated at varying periods at 300°. The mixture of benzamide and ammonium benzoate was analyzed by the method outlined by Reid.¹⁶ No difference was observed in the rate of hydrolysis of the amide, with or without gel.

Similar experiments were performed using ammonium acetate (at 150°). The rate of formation of acetamide was the same, with and without the gel.

¹⁶ Reid, *Am. Chem. J.*, **44**, 76 (1910).

A solution of 100 g. of ammonium carbonate in 200 cc. of glacial acetic acid was divided into two equal portions, 5 g. of activated silica gel being added to one of them. These were refluxed side by side and at suitable intervals exact portions drawn off from each and analyzed. The rate of formation of amide was the same in both cases.

Summary

The formation of nitriles from acid or ester vapors mixed with an excess of ammonia in the presence of silica gel has been studied.

From the acids the following yields were obtained: methyl cyanide, 95%; ethyl cyanide, 85%; *n*-propyl cyanide, 90%; *n*-butyl cyanide, 80%; isobutyl cyanide, 94%; *n*-pentyl cyanide, 90%; *n*-hexyl cyanide, 93%; *n*-undecyl cyanide, 55%; benzyl cyanide, 87%; phenylethyl cyanide, 81%. No cyanide was obtained from palmitic acid.

From the esters the following yields were obtained: methyl cyanide, 87%; *n*-propyl cyanide, 75%; phenyl cyanide, 77%.

The life of the catalyst is long in the case of the acids and short in the case of the esters.

The optimum operating temperature for the reaction is 500°.

The catalyst is only active in dehydrating amides, and is not effective in the establishment of the ammonia-acid, amide-water equilibrium.

Silica gel is by far the best catalyst for the reaction that has, as yet, been studied.

THE DECOMPOSITION OF KETONES IN THE PRESENCE OF SILICA GEL

The decomposition of ketones in the presence of various dehydrating catalysts has been rather widely studied. Acetone has received the most attention, the condensation products being particularly well investigated.

Acetone kept for a long time over lime or aluminum chloride is transformed into mesityl oxide and phorone.¹ By passing acetone vapors over catalysts heated at a suitable temperature, thoria and alumina usually being employed, mesityl oxide, phorone, etc., have been obtained.² Ipatiew

¹ Sabatier-Reid, "Catalysis in Organic Chemistry," D. Van Nostrand Co., New York, 1923, p. 287.

² (a) Fittig, *Ann.*, **110**, 23 (1859); (b) Beilstein and Reith, *ibid.*, **126**, 245 (1863); (c) Paulow, *ibid.*, **188**, 128 (1877); (d) Louise, *Bull. soc. chim.*, [2] **39**, 522 (1883); (e) Senderens, *ibid.*, [4] **3**, 824 (1908); *Compt. rend.*, **146**, 1212 (1908); (f) Mailhe and de Godon, *Bull. soc. chim.*, [4] **21**, 63 (1917).

and Petrow³ reported that mesitylene is the main product formed in heating acetone with dehydrating catalysts at high temperatures and pressures. Greene⁴ produced hexamethylbenzene, but no mesitylene, by heating acetone with zinc chloride. Reckleben and Scheiber⁵ prepared hexamethylbenzene by leading a mixture of acetone and methyl alcohol over alumina at 400° and assumed that the mechanism of the reaction involved the intermediate formation of mesitylene. Contrary to this, Senderens^{2e} reported that no mesitylene is formed from acetone with alumina.

Mesitylene, mesityl oxide, phorone, etc., are produced by distilling acetone with reagents such as sulfuric acid,⁶ or boron trifluoride.⁷ Heated with acetic anhydride, mesityl oxide is produced.⁸ The formation of mesityl oxide is not confined to "dehydrating catalysts;" nickel, for example, yields this product.⁹

The gaseous products from the decomposition of acetone have received some little attention. With alumina Senderens^{2e} reports the formation of a little gas at 400° which is an equal mixture of carbon dioxide and monoxide and ethylene. Adkins¹ says that "pure acetone passed over heated freshly prepared alumina forms condensation products, only about 60% of the acetone passing through unchanged. No gaseous products are formed." With copper-alumina at 650° Mailhe¹⁰ obtained a gas containing 15% carbon monoxide, 30% methane and 55% hydrogen. Jacobsen¹¹ reported the formation of aromatic hydrocarbons, among them triethylbenzene, by treatment of methyl ethyl ketone with sulfuric acid but later work has shown that homologs of mesityl oxide and phorone only are produced by the catalytic condensation of methyl ethyl ketone.¹² Petrow¹³ has shown that under conditions of high temperature and pressure homologs of mesityl oxide and isophorone are formed with only a trace of triethylbenzene.

Acetophenone condenses to *s*-triphenylbenzene in the presence of various catalytic agents at room temperature;¹⁴ or simply by long refluxing.¹⁵

³ Ipatiew and Petrow, *Ber.*, **59**, 2035 (1926); **60**, 735 (1927).

⁴ Greene, *Bull. soc. chim.*, [2] **32**, 422 (1879).

⁵ Reckleben and Scheiber, *Ber.*, **46**, 2363 (1913).

⁶ See references given by Ekeley and Howe. *J. Am. Chem. Soc.*, **45**, 1917 (1923); also Orndorff and Young, *Am. Chem. J.*, **15**, 249 (1893); "Organic Syntheses," John Wiley & Sons, Inc., New York, 1922, Vol. II p. 45.

⁷ Gasselin, *Ann. chim.*, [7] **3**, 58 (1894).

⁸ Hoffman, *J. Am. Chem. Soc.*, **31**, 722 (1909).

⁹ Mailhe and de Godon, *Bull. soc. chim.*, [4] **21**, 61 (1917).

¹⁰ Mailhe, *Mat. Grass.*, **14**, 6223, 6247 (1922); *Bull. soc. chim.*, [4] **31**, 863 (1922).

¹¹ Jacobsen, *Ber.*, **7**, 1435 (1874).

¹² Descude, *Ann. chim. phys.*, [7] **29**, 494 (1913); Schramm, *Ber.*, **16**, 1581 (1883); Ekeley and Howe, *J. Am. Chem. Soc.*, **45**, 1917 (1923).

¹³ Petrow, *Ber.*, **60**, 2548 (1927).

¹⁴ Engler and Berthold, *ibid.*, **7**, 1123 (1874); Reddelien, *Ann.*, **388**, 194, 173 (1912); *Ber.*, **46**, 2717 (1913); Odell and Hines, *J. Am. Chem. Soc.*, **35**, 82 (1913).

¹⁵ Engler and Dengler, *Ber.*, **26**, 1445 (1893).

Under conditions of high temperature and pressure, with alumina, tri-phenylbenzene, among numerous other materials, is produced.¹⁶

In the present investigation the decomposition of acetone, methyl ethyl ketone, and acetophenone has been studied in the presence of silica gel—particularly in connection with the condensation products formed.

Results

At atmospheric pressure and a temperature of 400–550° in the presence of silica gel the main condensation product of acetone is mesitylene, with a relatively small proportion of mesityl oxide, phorone, etc. At 500° a 17% yield of mesitylene is obtained. Silica gel seems to be the only dehydrating catalyst which in the gaseous phase converts acetone to mesitylene at ordinary pressures. Under conditions of high temperature and pressure silica gel also acts as an effective condensation catalyst. These conditions, however, favor the formation of high-boiling ketonic condensation products at the expense of low-boiling products including mesitylene. It is to be expected that high pressure would disfavor the mesitylene reaction since in this there is an increase in the number of molecules.

The method described here is advantageous for the preparation of mesitylene. The latter is readily isolated from the condensation product by washing with water and 70% alcohol, drying over calcium chloride and distilling, the fraction boiling between 130–190° being collected. The light-yellow oil thus obtained may be dried over sodium, which also effectively removes ketonic impurities, and subsequent fractionation yields a pure white oil of a high degree of purity.

The primary products in the homogeneous unimolecular decomposition of acetone are ketene and methane. The ketene then decomposes bimolecularly to ethylene and carbon monoxide.¹⁷ In the presence of silica gel at 460° the highest percentage yield of ketene produced was 4.4%, 65% of the acetone used being decomposed. The gas evolved at this temperature contained 9% carbon monoxide, 17% methane, 28% carbon dioxide, 40% unsaturated hydrocarbon and 3% hydrogen. These facts show that the homogeneous decomposition of acetone in the presence of silica gel is taking place to only a minor extent at the temperature employed.

The presence of a small amount of methylacetylene in the gaseous products would indicate that the mechanism of the formation of mesitylene is dehydration of the acetone to methylacetylene and polymerization of the latter. Sabatier and Kubota¹⁸ have assumed that the formation of mesitylene from allyl alcohol involves the intermediate formation of

¹⁶ Ipatiew and Petrow, *Ber.*, **60**, 1956 (1927).

¹⁷ Rice and Vollrath, *Proc. Nat. Acad. Sci.*, **15**, 702 (1929).

¹⁸ Sabatier and Kubota, *Compt. rend.*, **173**, 17 (1921).

methylacetylene. The fact that acetone passed over magnesium powder at a red heat produces magnesium methylacetylde¹⁹ shows that such a decomposition may occur.

Experiments so far, however, have not substantiated this deduction, for upon passing methylacetylene, produced from alcoholic potassium hydroxide and propylene bromide, over silica gel at temperatures between 400–500°, no mesitylene was isolated from the condensation product.

Methyl ethyl ketone does not condense to triethylbenzene in the presence of silica gel. Ketonic condensation products only are produced. This is in agreement with facts concerning the liquid phase condensation of the ketone—although sulfuric acid is effective in condensing acetone to mesitylene it will not convert methyl ethyl ketone to triethylbenzene. Furthermore, a comparison of the gaseous decomposition products of acetone and methyl ethyl ketone indicates that the two reactions are of a strikingly different nature.

Acetophenone, in the presence of silica gel, condenses in a manner similar to acetone, *s*-triphenylbenzene being formed.

Experimental

The apparatus employed was similar to that used in the work described in the preceding article.²⁰ The catalyst was 100 g. of activated silica gel.

Acetone Condensation Products.—An examination of the condensation product indicated that it consisted for the most part of water, unchanged acetone and mesitylene with small proportions of mesityl oxide, phorone, etc. An idea of the relative amounts of the constituents may be obtained by the results of a typical first fractionation (run at 430°): total condensation product 14 g.: 110–160°, 2 g.; 160–170°, 7 g.; 170–180°, 2 g.

The product from the acetone was washed with water, the upper layer separated, dried over calcium chloride, and distilled in a long-necked Claisen flask. The boiling point rose rapidly to 160° and the fraction boiling between 160 and 170° was taken as mesitylene.

The mesitylene was identified as the trinitro derivative.²¹ Nitration of the fractions below and above 160–170° showed that they contained considerable mesitylene.

Although the mesitylene fraction was taken between a fairly wide range, ten degrees, the fact that the lower and higher fractions contained considerable of the hydrocarbon would indicate that it is not over-estimated—although, undoubtedly, the ten degree fraction is not pure mesitylene. The yields of mesitylene are indicated in Table I.

¹⁹ Keiser, *Am. Chem. J.*, **18**, 329 (1896).

²⁰ Mitchell and Reid, *J. Am. Chem. Soc.*, **53**, 321 (1931).

²¹ Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, 1914, Vol. I, p. 201.

TABLE I
 YIELDS OF MESITYLENE

Temp., °C.	Acetone used, g.	Rate of flow, cc./min.	Yield, g.	Yield, %
430	80	0.90	4.30	7.8
450	80	.75	6.65	12.0
500	40	...	3.82	13.9
500	40	.75	4.72	17.2
500	40	.75	3.40	12.4
500	120	1.00	10.40	12.6
500	120	0.75	11.71	14.2
500	80	.65	7.60	13.8
550	80	.75	6.59	11.9

Condensation products other than mesitylene were further fractionated and examined. The results are summarized in Table II.

 TABLE II
 OTHER CONDENSATION PRODUCTS

Fraction	Determined	Density, 25/25 Ipatiew and Petrow	Chief constituent	Density, 25/25 Pure compound
127-131°	0.828	0.828	Mesityl oxide	0.854
162-167°	.861	.857	Mesitylene	.862
192-200°	.891	.871	Phorone	.877
205-210°	.918	.896	Isophorone	.925
248-253°	.941	.922	Xylitone	.936 ₄ ⁶

Mesityl oxide was further identified as the semicarbazone. Attempts to prepare the bromination product of the phorone (liquid) and the semicarbazone of the isophorone fractions were unsuccessful.

The mesitylene and xylitone fractions were only slightly soluble in 70% alcohol, while the others were readily soluble.

Experiments were performed under conditions of high temperature and pressure with silica gel, using the technique and equipment described by Herndon and Reid,²² the products being treated as in the experiments at atmospheric pressure. The results of the first fractionation of the product obtained (50 cc. of acetone was heated for two hours with 5 g. of activated gel in bombs of 100-cc. capacity) are as follows

	At 350°, g.	At 400°, g.	At 350° without catalyst, g.
Acetone used	160	192	160
Fraction 100-160°	11	7	4
Fraction 160-170°	10	5	1
Fraction 170-220°	6	13	2
Residue	13	20	4

At 350° a small amount of gaseous products was formed.

²² Herndon and Reid, *J. Am. Chem. Soc.*, 3065 (1928).

Unchanged Acetone and Ketene.—Unchanged acetone and ketene were estimated as follows. A suitable aliquot of the aqueous condensation product, collected in two traps immersed in ice-salt baths and washed into a volumetric flask, was titrated with standard sodium hydroxide for acetic acid and from this the proportion of ketene calculated. Any ketene escaping the receivers was bubbled into a flask containing hot water (to decrease the solubility of the carbon dioxide) and estimated as before by titration. The unchanged acetone was determined by adding an excess of hydroxylamine hydrochloride to a second aliquot part and titrating the liberated hydrochloric acid with standard sodium hydroxide,²³ a correction being made for the acetic acid formed from the ketene.

TABLE III
EXPERIMENTAL DATA

Temp., °C.	Acetone used, g.	Rate of flow, cc./min.	Ketene, %	Unchanged acetone
470	3.95	0.66	2.3	19
500	3.95	.66	2.6	18
490	4.35	.66	2.0	15
500	3.95	.66	2.2	17
410	3.95	.57	2.0	37
410	4.74	1.00	2.5	49
460	5.28	0.66	4.4	35
460	4.35	1.00	3.1	43
500	3.95	0.66	2.4	32
500	4.50	.80	2.5	30
500	3.95	1.25	2.1	52
500	3.95	0.66	2.6	33

Gaseous Products.—The gaseous products from the reaction were analyzed in an Orsat-Williams apparatus—the gases being collected over water saturated with the gas. Representative analyses of the gases produced are indicated in Table IV. Saturated hydrocarbon was calculated as methane.

TABLE IV
REPRESENTATIVE ANALYSES

Temp., °C.	Acetone, g.	Rate of flow, cc./min.	Gas evol., cc.	Percentages—				
				CO ₂	Unsat.	CO	H ₂	CH ₄
400	20.0	0.66	550	24.0	46.6	7.4	0	16.7
470	6.0	.66	400	28.0	40.0	9.2	3.2	17.0
450	8.0	.66	460	27.0	45.2	7.4	2.6	11.9
500	4.0	.66	350	26.8	44.7	7.5	3.0	
500	4.0	.66	400	25.0	43.5	8.7	2.7	

The presence of an acetylene hydrocarbon was thus shown: (1) a white precipitate was formed with mercuric sulfate acidified with sulfuric acid, (2) a cuprous salt was formed, soluble in ammoniacal ammonium chloride

²³ Allen, "Commercial Organic Analysis," 5th ed., 1923, Vol. I, p. 124.

(cuprous methylacetylide), (3) a silver salt was produced upon passing the gas through ammoniacal silver nitrate. The salts were decomposed by hydrochloric acid, evolving an unpleasant smelling gas.

Methyl Ethyl Ketone Condensation Products.—Upon passing the ketone over silica gel at 500° an oil insoluble in water, comparable in amount to that produced by acetone, was obtained.

From 140 g. of methyl ethyl ketone over 100 g. of commercial gel, at 500°, at the rate of 1.2 cc. per minute the following fractions were obtained: 110–145°, 1.9 g.; 145–160°, 1.2 g.; 160–170°, 0.8 g.; 170–210°, 1.6 g.; 210–220°, 1.5 g.; 220–300°, 4.9 g.; residue 5 g.

Heating 160 g. of the ketone in bombs, as in the acetone experiments, at 350° for two hours yielded the following fractions of condensation product, very little gas being formed: 110–150°, 1.2 g.; 150–170°, 8.5 g.; 170–205°, 7.5 g.; 205–225°, 3.5 g.; residue, 10 g. After further fractionation densities were determined:

Temp., °C.	Density 25/25		Chief constituent
	Determined	Petrow	
160–167	0.854	0.8534	Homo-mesityl oxide (peppermint-like odor)
205–220	.877	.9048	Homo-phorone
238–248	.919	.9435	Homo-isophorone
260–270	.939	.9492 ^a	Homo-isophorone

^a Density 20/4, Ekeley and Howe.

Any triethylbenzene obtained would be in the second fraction. Repeated attempts to nitrate portions of this material with a mixture of equal parts of nitric and sulfuric acids (heating for twenty minutes) were futile. In a few cases a few crystals, too few to handle, were obtained. Unsuccessful attempts were made to nitrate all fractions of the product.

Most of the product was soluble in 70% alcohol, which also indicates that the product consists mostly of ketonic substances similar to mesityl oxide and phorone.

Unchanged methyl ethyl ketone was estimated as in the acetone experiments. The results at 500° using 3.94 g. of the ketone are summarized.

Time, min.	Ketone undecomposed	% Decomposition
18.5	1.29	67.2
16.0	1.27	67.6
17.0	1.39	64.7
17.5	1.34	66.1

Gaseous Products.—The results of the analyses of the gaseous products are indicated in Table V.

Acetophenone.—Passing 156 g. of acetophenone over 100 g. of commercial gel at 500°, at the rate of 0.5 cc. per minute, produced 12 g. of *s*-triphenylbenzene (9.8% yield).

The product from the acetophenone experiments was distilled directly

TABLE V
RESULTS OF ANALYSES

Temp., °C.	Ketone used, g.	Rate of flow, cc./min.	Gas evol., cc.	Percentages				
				CO ₂	Unsat.	CO	H ₂	CH ₄
500	4.05	0.66	275	15.5	15	12	2.2	30
500	4.05	.66	300	22.2	17.3	16.5		
				20.2	16.4			

until unchanged acetophenone was almost completely removed. The residue was washed with 90% alcohol, dissolved in benzene, filtered, the benzene removed by evaporation and the product taken up in ether. By spontaneous evaporation large, dark yellow crystals were obtained; these were removed while a good deal of mother liquor was still present, washed with dilute alcohol, and recrystallized from acetic acid. Several recrystallizations yielded a pure sample of triphenylbenzene, which was further identified as the monobromo derivative.

Upon heating acetophenone in the bombs at 350° a great variety of products was obtained. No triphenylbenzene was isolated from the viscous high-boiling fraction following the procedure previously described or after fractionation of the material under high vacuum.

Summary

1. The principal condensation product of acetone, in the presence of silica gel at 400–550°, is mesitylene. This is the only catalyst that has effected this reaction at atmospheric pressure. The yields of mesitylene are comparable to those obtained by any other method.
2. It is suggested that the mechanism of the reaction involves dehydration of acetone to methylacetylene with subsequent polymerization of the latter to mesitylene. Experiments so far, however, have not substantiated this.
3. An analogous reaction does not take place with methyl ethyl ketone to an appreciable extent.
4. An analogous reaction takes place with acetophenone, yielding *s*-triphenylbenzene.

THE DECOMPOSITION OF ACETIC ACID IN THE PRESENCE OF SILICA GEL

The decomposition of acetic acid under the influence of various basic dehydrating catalysts has been well investigated, particularly in connection with the production of acetone, an excellent example of an "intermediate compound" catalytic reaction.

Chemically inert catalysts have been studied to some extent. Nef¹ observed that a high percentage of carbon monoxide was formed when acetic acid was passed over pumice at 500° and identified acetone as a minor product. Finely divided copper is also effective in converting acetic acid to acetone.² Senderens and Aboulenc,³ upon passing acetic acid over charcoal, found that the gases produced contained 21.5% carbon dioxide and 35.5% carbon monoxide. The liquid product contained traces of ketone and aldehyde. Senderens⁴ observed that when acetic acid was passed over precipitated silica, at 420°, among other materials, a gas was produced containing 90% carbon dioxide.

Kultashev and Kudryasheva⁵ reported that over charcoal at 300° appreciable decomposition of acetic acid occurred, increasing with rise in temperature, acetone and methane being two of the products.

Results

In passing acetic acid over silica gel the maximum yield of acetone is obtained at 430–460° (about 29%). Above this temperature the increased amount of acetone decomposed more than offsets the increased amount of acetone formed. Above 400° appreciable decomposition of the acetone formed becomes noticeable. A small amount of an insoluble oil is obtained similar to that produced in the decomposition of pure acetone. Results are summarized in Table I.

In Experiments 19–24 aqueous acetic acid was used. It is evident that with aqueous acid a greater proportion of the decomposed acid is obtained as acetone. This would indicate that the proportion of water vapor present influences the rate of decomposition of the acetone—in accord with the results of Kultashev and Kudryasheva.⁵ In Experiments 25–26 the same catalyst was used with glacial acetic acid.

¹ Nef, *Ann.*, **318**, 221 (1901).

² Sabatier-Reid, "Catalysis in Organic Chemistry," D. Van Nostrand Co., New York, 1923, p. 299.

³ Senderens and Aboulenc, *Compt. rend.*, **170**, 1064 (1920).

⁴ Senderens, *Bull. soc. chim.*, [4] **3**, 823 (1908).

⁵ Kultashev and Kudryasheva, *Chem. Abstracts*, **19**, 2443 (1925); *J. Russ. Phys.-Chem. Soc.*, **55**, 383 (1924).

TABLE I
EXPERIMENTAL RESULTS

Expt.	Catalyst	Temp., °C.	Time, min.	% Acid decomposed	% Yield acetone Based on acid used	Based on acid decomposed
1	A	400	22	41.3	13.8	33.4
2		428	25	66.0	15.1	22.9
3		428	17	60.9	15.0	24.6
4		455	23	78.1	27.9	35.7
5		495	29	87.5	18.1	20.7
6		405	26	62.1	5.5	8.9
7		428	22	60.7	12.4	20.4
8		458	13	50.4	22.9	45.5
9		500	23	78.9	23.6	30.0
10	B	360	23	55.9	3.2	5.7
11		402	20	32.2	13.6	42.2
12		402	33	41.0	17.5	42.7
13		432	23	44.9	27.9	62.0
14		462	21	65.6	27.8	42.5
15		492	21	81.8	17.4	12.3
16		415	21	61.6	6.5	10.6
17		440	21	47.3	24.4	51.6
18		520	25	81.0	20.4	25.2
19	B Using aqueous acetic acid	400	20	27.1	12.8	47.2
20		427	19	37.8	23.7	62.7
21		420	17	31.0	14.5	45.7
22		427	19	29.2	19.2	65.7
23		401	18	21.6	12.8	59.2
24		401	19	25.2	11.6	46.0
25		401	23	29.1	13.0	44.7
26		401	23	28.9	13.4	46.4
27	C	401	20	35.8	9.6	26.8
28		401	13	25.9	9.4	36.3
29		401	9	18.0	8.6	47.8
30		428	23	33.2	17.5	52.7
31		428	..	32.6	18.4	56.5
32	D	402	20	35.2	12.0	34.1
33		401	31	30.4	17.1	56.2
34		434	21	37.8	25.7	68.0

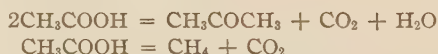
The acid used in each experiment was 5.114 g. Experiments 1-9, using commercial gel, catalyst A, cover a larger number of experiments and the last results therefore represent those obtained after considerable use of the catalyst. In Experiments 10-18 a fresh charge of commercial gel was used, catalyst B. In Experiments 19-24 aqueous acetic acid was used; 19 and 20 contained 4.0%; 21-23, 8.0%; 24, 2.0% water by weight. Experiments 25 and 26 were run on the same catalyst using glacial acetic acid. Experiments 27-31 were run on a sample of electrolytically purified gel after a short period of activation, namely, one hour at 200° and one hour at 450°, catalyst C. Experiments 32-34 were run on purified gel after the usual period of activation, catalyst D.

Purified gel and commercial gel are equally effective catalysts in the formation of acetone (Experiments 32-34).

Experiments 27–31, using gel activated for a short time, clearly indicate that the conditions of activation of the catalyst considerably influence its activity. Experiments 27–29 show that as the rate of passage of the acid is increased, although the actual yield of acetone is decreased, the yield based on the acid decomposed is increased—hurrying the material through the tube greatly decreases the amount of acetone decomposed.

The activity of the catalyst slowly decreased with use as appears from the results of Experiments 1–9, which cover a catalyst that had been used for quite a time. In this connection it is interesting to note that the gel is almost immediately blackened in this reaction, while in the nitrile reaction—using ammonia and acetic acid—at the same temperatures,⁶ blackening of the gel takes place very slowly. The shining, jet-black gel is so completely impregnated with carbon that it cannot be burned out except on the outer surface at a red heat in a current of oxygen.

It is possible for acetic acid to decompose in two ways, in both of which carbon dioxide is produced



The results indicated in Table II, which involve the precise determination of carbon dioxide liberated in the reaction, clearly indicate that not all of the carbon dioxide liberated is obtained from the acetone reaction—some is obtained from the splitting of acetic acid into methane and carbon dioxide.

TABLE II
RESULTS OF EXPERIMENTS

No.	Catalyst	Temp., °C.	Weight of carbon dioxide, g.
1	A	400	0.880
2		450	1.116
3		450	1.206
4		450	1.161
5	B	500	1.508
6		500	1.130
7	C	300	0.000
8		350	.050
9	D	380	.386
10		400	.428
11		450	.580
12		500	1.285
13		500	1.046

Acetic acid (4.78 g. in each experiment) was passed over the gel at the rate of 0.2 cc. a minute. In order to make a correction for any carbon dioxide liberated in the decomposition of the acetone formed, blanks were run on pure acetone and the following corrections were subtracted from the amount of carbon dioxide found: at 400°, 0.024 g.; 450°, 0.044 g.; 500°, 0.054 g. The values given in the table are these corrected values.

⁶ Mitchell and Reid, *J. Am. Chem. Soc.*, **53**, 321 (1931).

Experiment 6 was run after a large amount of acid (100 cc.) had been passed over the gel of Experiment 5.

Considering average results, a summary is made in the following table

Temp., °C.	Acetone obtained, %	Methane produced if no acetone decomposed, %	HAc actually decomposed, %	Decomp. acid to acetone, %
400	14	18	37	65
450	28	19	65	85
500	24	28	81	90

The figures under "acetone obtained" are taken from Column 6 of Table I. Those in the next column are calculated from Table II by assuming that no acetone is decomposed after it has once been formed—the carbon dioxide corresponding to 14, 28 and 24% acetone being subtracted from the total carbon dioxide evolved, the remainder indicating the methane produced. It is evident that the sum of the figures of the second and third columns should equal the amount of acetic acid known to be decomposed, which was determined by titration (Table I). The difference between this sum and the acetic acid actually decomposed and the fact that the acetone reaction involves two molecules of acetic acid, whereas the methane reaction involves only one, makes it possible to estimate the amount of acetone decomposed under the conditions of the experiments and also, of course, the extent of the methane reaction.⁷

The conclusion is reached that 40 to 60% of the acetone originally formed in the reaction is decomposed—more, of course, being decomposed at the higher temperature. The acetone reaction is the predominant one. The estimate of the fraction of decomposed acid that is converted to acetone is given in the last column of the table.

This is in fair accord with the observation that acetone is decomposed to a similar extent in the presence of silica gel, using comparable rates of flow.

A comparison of the analyses of the gaseous products in the passage of acetic acid (Table III), and acetone⁸ over silica gel clearly indicates that the methane reaction is occurring to some extent—and the results agree in a general way with conclusions already deduced. Moreover, the analysis of the gases from acetic acid shows (1) that at lower temperatures the gas is richer in carbon dioxide (less acetone is decomposed), (2) that the amount of carbon dioxide evolved (and therefore acetone formed) decreases as the catalyst is used. Experiment 6, Table II, which was run on the

⁷ The decomposition into ketene and water would probably not occur to any great extent at these temperatures—Hurd and Martin, *J. Am. Chem. Soc.*, **51**, 3614 (1929). Any attempt to estimate the extent of this reaction by isolating the ketene, or estimating acetic anhydride formed, would be meaningless as ketene is also formed from the decomposition of the acetone. In fact, it may not be unreasonable to suppose that the formation of acetone is the intermediate step in the decomposition of acetic acid to ketene.

⁸ Mitchell and Reid, *ibid.*, **53**, 330 (1931).

same catalyst as in 5, passing 100 cc. of acid between experiments, precisely confirms this observation.

TABLE III
EXPERIMENTAL DATA

Temp., °C.	Acid used, g.	Rate of flow cc./min.	Gas evol., cc.	Percentage of					
				CO ₂	Unsat.	CO	O ₂	H ₂	CH ₄
500	5.25	0.80	1700	47.5	7.5	9.0	2.0		
500	2.10	.80	600	42.5	7.0	22.5	0.5		
400	10.50	.80	150	52.2	2.6	18.4	1.8		
450	5.25	.80	450	50.5	4.5	22.1	0.5	2.2	20.2
500	2.10	.80	..	38.0	3.8	25.6	0.2	9.4	22.7
425	5.25	.56	175	63.0	8.5	6.5			20.0
460	3.15	.50	375	45.5	5.0	9.5			

Senderens' analysis⁴ of the gaseous product obtained in passing acetic acid over precipitated silica, at 420°, indicated that it consisted of 90% carbon dioxide, and as the other 10%, consisting of carbon monoxide and a little ethylene, could be considered as decomposition products of the acetone produced, he concluded that the methane reaction did not occur.

The fact that silica gel, a chemically inert catalyst, is so effective in the conversion of acetic acid to acetone (85% of the acetic acid decomposed being converted into acetone) is hardly to be expected from the intermediate compound theory.

Experimental

The apparatus employed was similar to that described in the preceding article.⁸ The catalyst, 100 g. of silica gel, was activated by heating for three hours at 210° and three hours at 450–500° in a slow current of air, dried with calcium chloride. A weighed quantity of the acid was passed through the dropping arrangement, through a capillary, and thence over the gel, through a condenser cooled by a rapid current of water and the product collected in a receiver immersed in carbon dioxide snow. An all-glass apparatus was employed—eliminating all rubber connections as well as "pockets" in which acid or product might be trapped. After passing the acetic acid over the catalyst the apparatus was swept out with nitrogen. The product was washed into a 50-cc. volumetric flask, a 2-cc. aliquot titrated for acetone by Messinger's method⁹ and a 5-cc. aliquot titrated for unchanged acid with standard sodium hydroxide.

The exact determinations of carbon dioxide were made by passing the gases evolved from a weighed portion of acid through a condenser, an ice-salt trap, a small bubble tube containing water, a carbon dioxide snow-acetone trap, drying tubes and weighed soda-lime tubes. The tubes were brought to constant weight before and after the run, using a current of dried nitrogen.

⁹ Scott, "Standard Methods of Chemical Analysis," Vol. II, p. 1537, 1922.

The gas produced was analyzed in an Orsat-Williams apparatus, being collected over water previously saturated with the gas. The saturated hydrocarbon was calculated as methane.

Summary

The decomposition of acetic acid in the presence of silica gel at a temperature range of 400–500° has been studied.

Silica gel is an effective catalyst for the conversion of acetic acid to acetone. At least 85% of the acetic acid decomposed in the presence of silica gel produces acetone.

BIOGRAPHY

James Albert Mitchell, the author of this dissertation, was born at Baltimore, Md., June 10, 1906. He received his early education in the public and high schools of Catonsville, Md. In October 1923 he entered the Engineering School of the Johns Hopkins University and received the degree of Bachelor of Science in Chemistry in June 1927. In October 1927 he entered the Graduate Department of Chemistry of the Johns Hopkins University where he was engaged in graduate work for three years. During the years 1927-28 and 1928-29 he was Student Assistant in Chemistry and held the Du Pont Fellowship in 1929-30.

